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D-81675 München (DE)**(54) **Solid oxide electrolyte fuel cell.**

(57) A solid oxide electrolyte fuel cell comprises a power generation film consisting of a solid oxide electrolyte film dimpled on almost whole area on both sides thereof, an oxygen electrode formed on one side thereof, and a fuel electrode formed on the other side of thereof, and comprises a pair of inter-connectors located on both sides of the power generation film. Furthermore, this invention adopts a seal structure for sealing each side of the power generation film and each of the corresponding inter-connector to achieve the above-described object. The peripheral area on the power generation film to form a seal face with the interconnector is formed to have an almost the same plane with that of the dimpled pattern formed on the power generation film, and the provided seal section has almost the same thermal expansion coefficient with the solid

oxide electrolyte film which forms the power generation film.

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BACKGROUND OF THE INVENTION

1. Industrial Field of the Invention

This invention relates to a solid oxide electrolyte fuel cell (hereinafter referred to simply as "SOFC"), and more particularly to an SOFC which is applicable to an electrolytic cell in water electrolysis and CO₂ electrolysis, as well as to power generation.

2. Description of the Related Art

A typical example of a conventional plate type SOFC is shown in Figs. 3 and 4. Fig. 3 shows a perspective view of disassembly of the conventional plate type SOFC, and Fig. 4 shows a perspective view of the assembly thereof. In the figures, the reference numeral 1 denotes a power generation film consisting of a solid oxide electrolyte film 2, an oxygen electrode 3, which is provided on the upper surface of the solid oxide electrolyte film 2, and a fuel electrode (not shown), which is provided on the under surface of the solid oxide electrolyte film 2.

An interconnector 6 is provided on the upper surface of the power generation film 1 through a corrugated air electrode side support 4 and packings 5,5, divided into two pieces to hold the air electrode side support 4 from both sides. When laminated, the air electrode side support 4 is held between the packings 5,5.

Further, the reference numeral 7 denotes an air inlet provided at the side gap of the packings 5,5. An air outlet (not shown) is provided at the other side gap of the packings 5,5, opposed to the air inlet 7.

Furthermore, on the under surface of the power generation film 1, there is provided an interconnector 10 through a fuel electrode side support 8 having a corrugated shape in perpendicular direction against the air electrode side support 4, and packings 9,9, divided into two pieces to hold the fuel electrode side support 8 from both sides. Accordingly, when laminated, the fuel electrode side support 8 is held between the packings 9,9. The reference numerals 11 and 12 denote a fuel inlet and a fuel outlet, respectively, provided at the both side gaps between the packings 9,9.

The flow of fuel is a perpendicular direction to that of air, that is, the fuel is introduced from the inlet 11 and flows into the fuel outlet 12 through the both surfaces of the fuel electrode side support 8, and air is introduced from the air inlet 7 and flows into the air outlet (not shown) through the both surfaces of the air electrode side support 4.

Thus formed cell is generally laminated to several layers to increase an output. That is, to in-

crease the output, air electrode side components such as packings 5,5 and an air electrode side support 4 are mounted on the under surface of the interconnector 10, and an oxygen electrode 3 of a power generation film 1 is provided under the air electrode side components, furthermore fuel electrode side components such as packings 9,9 and a fuel electrode side support 8 are mounted on the upper surface of interconnector 6, and a fuel electrode of power generation film 1 is provided above the fuel electrode side components. In this manner, the lamination succeeds to increase the output.

As described above, a conventional SOFC needs to be provided with supports 4, 8, and packings 5,5 and 9,9 at air electrode side and fuel electrode side, respectively, other than the power generation film 1 and interconnectors 6, 10. The configuration increases the number of components, which increases the work steps to fabricate components and which takes a time for assembling a cell. To solve the problems, an invention which eliminated the supports 4, 8, was disclosed in Japanese Patent Application Hei 5-6048 of "Solid Oxide Electrolyte Fuel Cell", filed by the applicant of the present invention. The above invention is characterized by an electrical joint of a power generation film having a dimpled pattern with an interconnector.

The disclosed invention has, however, the following problems.

(1) Packings which hold a power generation film having a dimpled pattern are necessary to be disposed between interconnectors as illustrated in Figs. 3 and 4. If the packings are made from a rigid material, extremely an accuracy in the height of the individual dimples on the power generation film is required. However, such an accuracy is extremely difficult to obtain in the present processing technology for the power generation film. If the packings are fabricated by a soft material, various problems arise caused by the gas permeability of the packings itself.

(2) Further, in the type shown in Figs. 3 and 4, which introduces and discharges air and fuel from both sides of the cell, the air inlet 7 and outlet are necessary to be newly added, compared with the type illustrated in Fig. 5 where the air is introduced and discharged from top and bottom of the cell. In addition, a solid oxide electrolyte film is required to reduce its thickness to increase the ion conductivity. A thin structure may induce a problem of strength at the openings of air inlet and outlet. As a result, the openings are necessary to be reinforced using a support such as round tube. The countermeasures increases the number of components and increases time for fabricating and assembling them.

(3) Conventional configuration requires the power generation film to have a flat shape at the region sandwiched by packings even though the power generation film is dimpled as a whole. The requirement makes the fabrication of power generation film further difficult because the power generation film contracts to approximately 70% during firing process compared with that before firing to have a specified cell.

(Object of the Invention)

The object of the invention is to solve the problems described above and to provide a solid oxide electrolyte fuel cell which does not need special packing and which simplifies the manufacturing method on the manufacturing process thereof. Moreover, even when air and fuel are introduced and discharged from the sides of the cell, the openings as the inlet and outlet do not need special support.

SUMMARY OF THE INVENTION

A solid oxide electrolyte fuel cell comprises a power generation film consisting of a solid oxide electrolyte film dimpled on almost whole area on both sides thereof, an oxygen electrode formed on one side thereof, and a fuel electrode formed on the other side thereof, and comprises a pair of interconnectors provided on both sides of the power generation film. Furthermore, this invention adopts a seal structure for sealing each side of the power generation film and each of the corresponding interconnector to achieve the above-described object.

The peripheral area on the power generation film to form a seal face with the interconnector is formed to have an almost the same plane with that of the dimpled pattern formed on the power generation film, and the provided seal section has almost the same thermal expansion coefficient with the solid oxide electrolyte film which forms the power generation film.

According to the invention, the solid oxide electrolyte film is processed to have a dimpled pattern on almost whole surface area thereof, and is calcined. After calcination, considering the thermal expansion coefficient, a slurry of a material same as the solid oxide electrolyte film or of a mixture with the material of interconnector, or of a material similar to them is filled in the concave zone for forming a gas tight zone, and is fired to form a seal section. The joint with interconnector is performed by either one of the following major two methods.

(1) Jointing with an adhesive (normally a glass adhesive is used). (2) Diffusion jointing which is conducted by pressing and heating the seal

section during complete firing stage.

With the above means, an SOFC having a simplified cell structure and improved reliability is obtained.

Since this invention uses a solvent and a curing agent as well as YSZ fine particles during the preparation process of the solid oxide electrolyte film used in an SOFC, the green shape contracts at an approximate degree of 30% during the complete firing stage.

This invention provides an SOFC which does not need special packing and which simplifies the manufacturing method for manufacturing process thereof, and even when air and fuel are introduced to and discharged from the sides of the cell, the openings for the inlet and outlet of air and fuel do not need special support.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an explanatory drawing of SOFC of an example of this invention. Fig. 1(A) is a perspective view of a disassembled SOFC. Fig. 1(B) is a cross-sectional view of the power generation film of Fig. 1(A) along X-X line.

Fig. 2 is an assembled drawing of SOFC of Fig. 1. Fig. 2(A) is a cross-sectional view of the SOFC after laminated. Fig. 2(B) is the view X of Fig. 2(A). Fig. 2(D) is the view Y of Fig. 2(A). Fig. 2(C) is the view Z of Fig. 2(B).

Fig. 3 is a perspective view of a disassembled SOFC of prior art.

Fig. 4 is a perspective view of assembled SOFC of Fig. 3.

Fig. 5 is a perspective view of disassembled SOFC of other type of prior art.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A preferred embodiment of this invention is described below with reference to the drawings.

In Fig. 1, the reference numeral 21 denotes a power generation film which consists of a solid oxide electrolyte film 22 provided with dimple convex zone 22a and dimple concave zone 22b on both sides thereof, a fuel electrode 23 and an oxygen electrode 24 formed on both sides of the solid oxide electrolyte film 22, respectively. The dimple convex zone 22a and the dimple concave zone 22b have almost similar shape. At the periphery of the power generation films 21, there are located seal sections 26 which form the seal faces 26a to seal between the interconnectors 25a, 25b, and 25c. The seal face 26a at the seal section 26 is smoothly shaped to keep almost same plane with the apex of the dimple convex zone 22a. The seal face 26a is made of a material having nearly

equal thermal expansion coefficient with the solid oxide electrolyte film 22.

The SOFC having the above-described structure is manufactured by the following procedure.

First, the solid oxide electrolyte film 22 is prepared. The fine particles of YSZ, a binder such as PVB, a plasticizer, a dispersant, and a solvent such as ethanol are blended together. The mixture is dried to form a flat green sheet using a doctor blade unit. The green sheet is molded in a die to give a specified dimple pattern, which is then subjected to a temporary calcination at approximately 1250 °C.

Next, the fuel electrode 23 is formed on one side of the prepared solid oxide electrolyte film 22. The material of the fuel electrode 23 is usually a Ni mixed with YSZ at a rate of 30% to 60% to the total quantity. The mixture is slurried and applied onto the one side of the solid oxide electrolyte film 22 at an approximate thickness of 50µm (after fired). After drying the applied mixture, it is fired. Since the firing temperature is 1400 °C, the firing is preferably conducted after the complete firing of the solid oxide electrolyte film 22. Further, the oxygen electrode is formed on the other side of the solid oxide electrolyte film 22. The material of oxygen electrode 24 is LSM mixed with YSM at a rate of 20% to the total quantity. In a similar manner with that of fuel electrode 23 preparation, the mixture of LSM and YSM is slurried and applied onto the other side of the solid oxide electrolyte film 22 at an approximate thickness of 50µm (after fired). After drying the applied mixture, it is fired. Since the firing temperature is 1300 °C, the firing may be conducted simultaneously with the heating of an adhesive or a dispersant on the seal face 26a described later.

Next is the formation of seal section at the periphery of power generation film 21 prepared by the above-described procedure. The seal section is prepared using a mixture similar with that used to form the solid oxide electrolyte film 22.

The seal section 26 has gaps at the points corresponding to the hydrogen inlet 27, the hydrogen outlet 28, the air inlet 29, and the air outlet 30. Since the passages of hydrogen and of air are formed crossing each other, the mixture is applied on both sides of the power generation film 21 at a dotted region in Fig. 2. Accordingly, each zone of hydrogen inlet 27, hydrogen outlet 28, air inlet 29, and air outlet 30 is formed by applying the mixture on only one side of the power generation film 21 and by securing smoothness using a pad plate for weight. After drying, the seal section is formed by firing at a temperature ranging from 1400 to 1500 °C.

Thus obtained state is shown in Fig. 1.

Then the seal face 26a is applied with an adhesive (glass group) or a dispersant (YSZ plus LSC used in interconnector), further applied with an adhesive for electrode at the dimple convex zone 22a and dimple concave zone 22b, which are then heated and pressurized at 1200 to 1300 °C to adhere or dispersedly joint integrally the power generation film 21 and the seal section 26 with the interconnectors 26a, 26b, and 26c.

As shown in Fig. 1 and Fig. 2, the SOFC of this embodiment has the structure having the power generation film 21 which consists of the solid oxide electrolyte film 22 provided with the dimple convex zone 22a and the dimple concave zone 22b for almost whole surface area on both sides thereof, the fuel electrode 23 and the oxygen electrode 21 formed on each side of the solid oxide electrolyte film 22, respectively, and consists of the interconnectors 25a through 25c located on both sides of the power generation film 21, and of the seal section 26 which is formed at the region to form the seal face at the periphery of power generation film 21 and between the interconnectors 25a through 25c and which is made from a material having almost equal thermal expansion coefficient with that of the solid oxide electrolyte film 22.

As a result, this invention provides the following effects.

The SOFC of this invention assures a highly accurate seal face, enables tight adhesion between the interconnectors 25a through 25c and the solid oxide electrolyte film 22, and improves the accuracy of adhesion between the electrode of the power generation film 21 and the interconnectors 25a through 25c, which provides a cell with high reliability.

As for the method to apply a solid oxide electrolyte film 22 with dimple pattern, the embodiment described above which applies the dimple pattern on almost the whole surface area significantly simplifies the manufacture of the solid oxide electrolyte film 22 compared with the conventional method which leaves a flat area to secure the seal face. The production yield of conventional method is only 30 to 50%, and the method described in the embodiment gives nearly 100%. Furthermore, since there is no need for mounting special component at the inlet and outlet of gases, the reliability of manufacturing process is improved and the number of processing manhours is reduced.

Since the pitch between dimples is relatively small at around 3mm and since a single solid oxide electrolyte film face contains lots of dimples, the height of each apex of dimple convex zone does not match each other in some cases. Consequently, if the packing is made of a rigid material for sandwiching a solid oxide electrolyte (power generation film) between interconnectors to joint them

together, then, there arises a problem in electric connection between the electrode and the interconnector. On the contrary, if the packing is made of a soft material, the packing itself allows gas to permeate. As a result, prior art accompanies various difficulties on sealing ability.

On the other hand, according to the embodiment described above, a solid oxide electrolyte film is firstly calcined, then a slurried material which has the same thermal expansion coefficient with that of the solid oxide electrolyte film, an YSZ or an LSC of the same material with the interconnector or their mixture in this case, is applied onto the specified seal face, and a pad plate is placed on the applied mixture layer to heat to completely fire. Thus a solid oxide electrolyte film provided with a seal face of uniform height over the whole surface area thereof is obtained.

Claims

1. A solid oxide electrolyte fuel cell characterized by comprising a power generation film consisting of a solid oxide electrolyte film provided with dimple pattern on both sides thereof, an oxygen electrode formed on one side of the solid oxide electrolyte film, and a fuel electrode formed on the other side of the solid oxide electrolyte film, and comprising a pair of interconnectors provided on both sides of the power generation film, wherein the power generation film 21 consists of a solid oxide electrolyte film 22 formed on almost the whole surface area on both sides thereof, and an oxygen electrode 24 and a fuel electrode 23 each of which is formed to match a shape of the solid oxide electrolyte film 22 on one side and on the other side thereof, respectively, and wherein there is provided a seal section 26 which is formed at a periphery of the power generation film 21 and at an area to form the seal section 26a between the interconnectors 25a, 25b, and 25c, and which is formed to have an almost the same plane with that of the dimples 22a, 22b, and which is made of a material having almost the same thermal expansion coefficient with the solid oxide electrolyte film 22.
2. A solid oxide electrolyte fuel cell as claimed in claim 1, characterized in that the seal section 26 is made of a material same as that of the solid oxide electrolyte film 22.
3. A solid oxide electrolyte fuel cell as claimed in claim 1, characterized in that the seal section 26 is made of a material same as that of the interconnectors 25a, 25b, and 25c.

4. A solid oxide electrolyte fuel cell as claimed in claim 1, characterized in that the seal face 26 is applied with an adhesive or a dispersant, and the convex zone 22a and the concave zone 22b of the dimple are applied with an adhesive for electrode to integrate the power generation film 21, the seal section 26, and the interconnectors 25a, 25b, 25c, together.

Fig. 1(A)

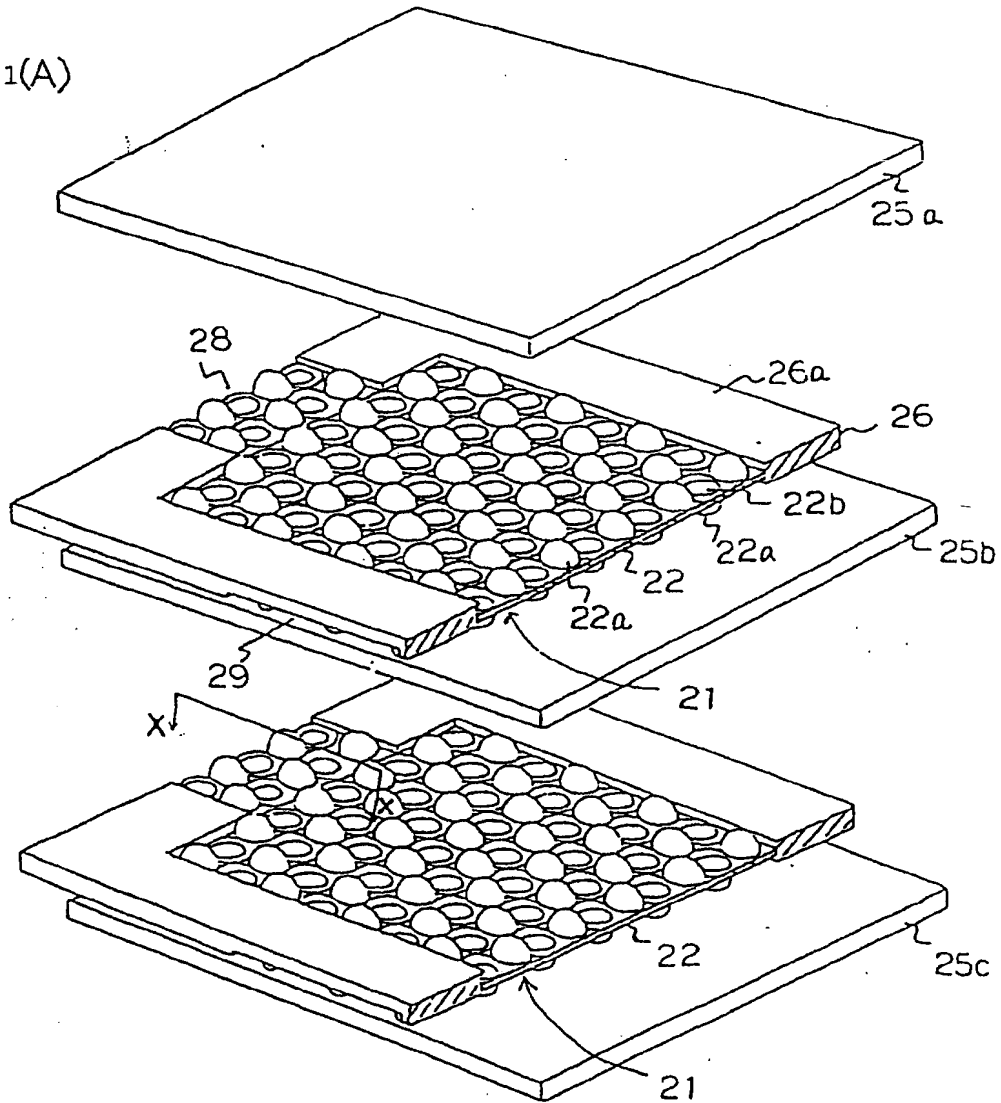
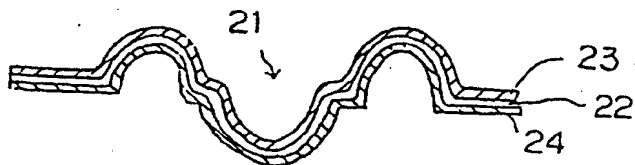


Fig. 1(B)



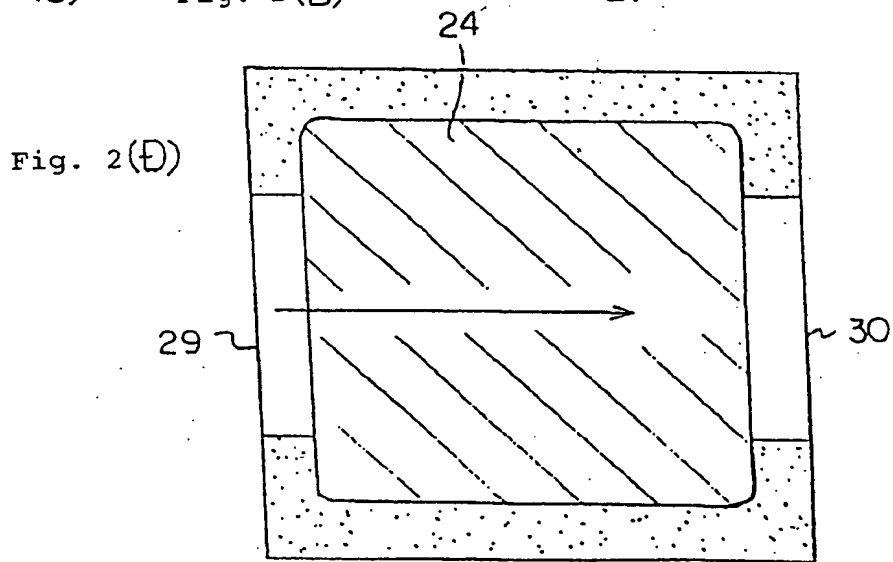
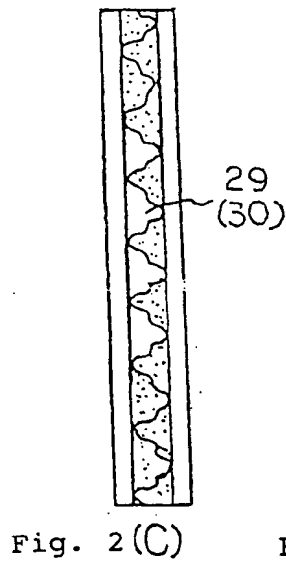
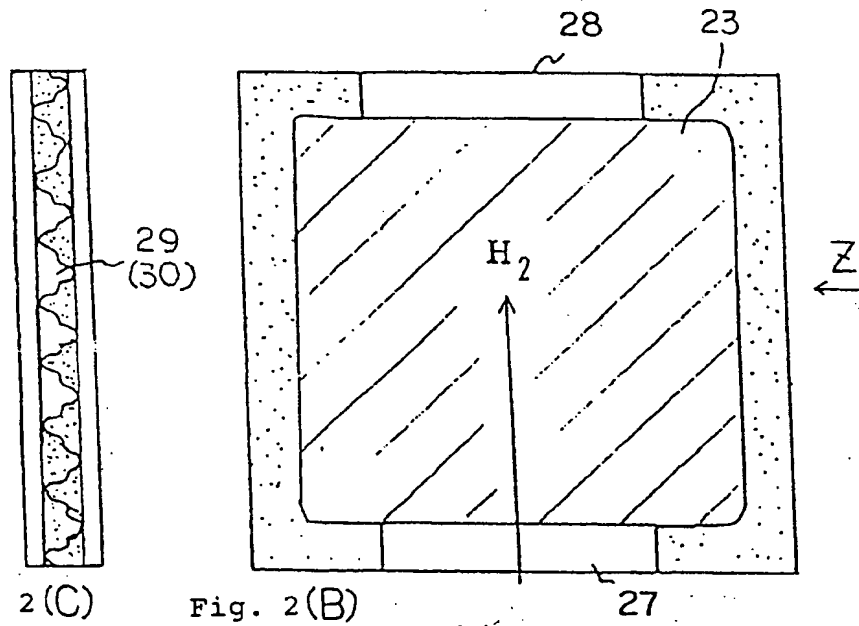
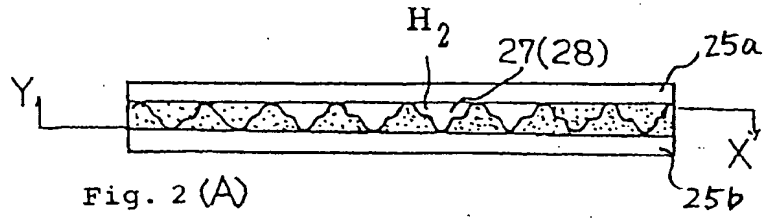


Fig. 3

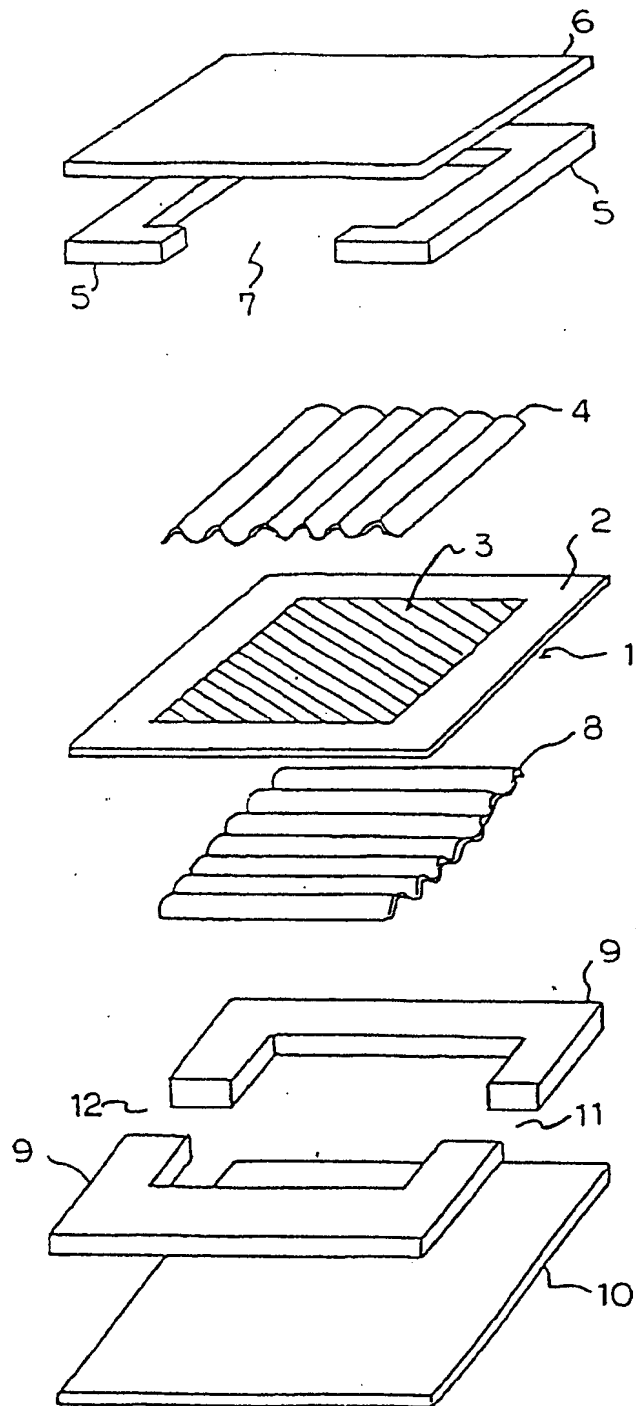


Fig. 4

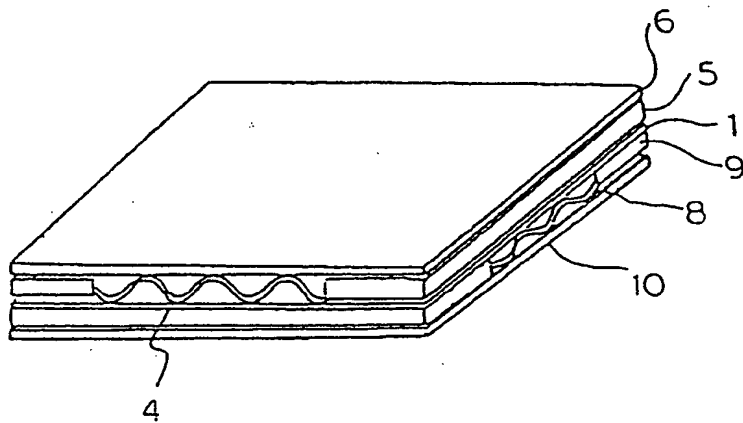
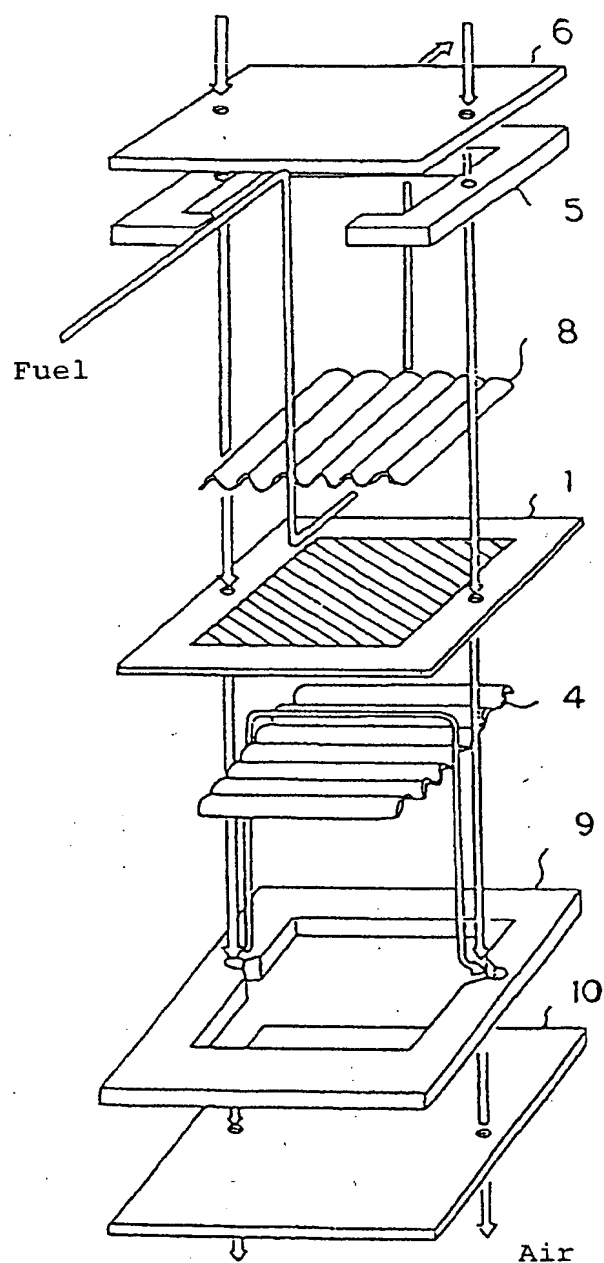


Fig. 5



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D-81675 München (DE)(54) **Solid oxide electrolyte fuel cell.**

(57) A solid oxide electrolyte fuel cell comprises a power generation film consisting of a solid oxide electrolyte film (22) dimpled (22a,22b) on almost whole area on both sides thereof, an oxygen electrode (24) formed on one side thereof, and a fuel electrode (23) formed on the other side of thereof, and comprises a pair of interconnectors (25a,25b,25c) located on both sides of the power generation film. Furthermore, this invention adopts a seal structure (26) (26a) for sealing each side of the power generation film and each of the corresponding interconnector to achieve the above-described object. The peripheral area on the power generation film to form a seal face with the interconnector is formed to have an almost the same plane with that of the dimpled pattern formed on the power genera-

tion film, and the provided seal section has almost the same thermal expansion coefficient with the solid oxide electrolyte film which forms the power generation film.

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Fig. 1(A)

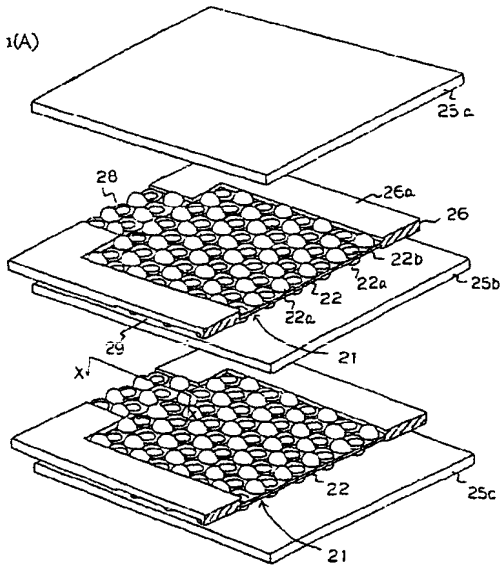
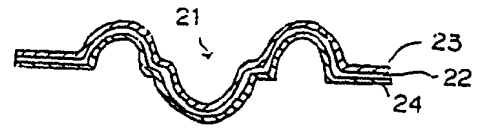


Fig. 1(B)





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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO-A-92 09116 (ALLIED-SIGNAL INC) 29 May 1992 * claims 1-3,9; figure 6 * * page 5, line 30 - page 6, line 5 * * page 4, line 20 - page 5; figures 2A-2D 3 *	1,2	H01M8/24 H01M8/02
D,Y	JP-U-04 008 259 (MITSUBISHI JUKOGYO KABUSHIKI KAISHA) * the whole document *	1,2	
A	PATENT ABSTRACTS OF JAPAN vol. 15 no. 40 (E-102) ,30 January 1991 & JP-A-02 276166 (TONEN CORP) 13 November 1990, * abstract *	1,2	
A	PATENT ABSTRACTS OF JAPAN vol. 15 no. 371 (E-1113) ,18 September 1991 & JP-A-03 147267 (SANYO ELECTRIC CO LTD) 24 June 1991, * abstract *	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01M
A	PATENT ABSTRACTS OF JAPAN vol. 13 no. 371 (E-807) ,17 August 1989 & JP-A-01 124964 (MITSUBISHI HEAVY IND LTD) 17 May 1989, * abstract; figure 3 *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 15 no. 315 (E-109) ,12 August 1991 & JP-A-03 116659 (FUJI ELECTRIC CO LTD) 17 May 1991, * abstract *	4	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 1995	Examiner D'hondt, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 14 no. 493 (E-0995) ,26 October 1990 & JP-A-02 204974 (MITSUBISHI HEAVY IND LTD) 14 August 1990, * abstract *	4	
A	US-A-4 857 420 (DONALD L MARICLE ET AL) * column 4, line 31 - line 40; figure 4 *	4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 1995	Examiner D'hondt, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			

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